
III.A.17 SOFC Cathode Materials Development at PNNL

Objectives

- Develop and optimize SOFC cathode electrode materials and microstructures offering low polarization losses and long-term stability at intermediate SOFC operating temperatures (650-800°C).
- Improve understanding of mechanisms affecting cathode performance, including both intrinsic (e.g., composition, microstructure) and extrinsic factors (e.g., Cr poisoning).

Accomplishments

- Electrically tested and characterized lanthanum strontium cobalt ferrite (LSCF) cathodes and developed underlying degradation mechanisms.
- Developed LSCF/Ag composite cathode material and architecture intended for SOFCs operating at ~650°C.
- Participated in a joint study with General Electric and Argonne National Laboratory (ANL) investigating Cr-related degradation in LSM cathodes.

Introduction

Minimization of cathodic polarization losses represents one of the greatest challenges to be overcome in obtaining high, stable power densities from SOFCs. Cathodic polarization typically exhibits high activation energy relative to other internal power losses, so the need to improve cathode performance becomes increasingly important as the targeted SOFC operating temperature is reduced. The severe environmental conditions experienced by the cathode during operation limit the number of likely candidate materials. In

particular, the cathode material must be stable at the SOFC operating temperature in air; and it must have high electronic conductivity, high catalytic activity for the oxygen reduction reaction, and a thermal expansion compatible with the SOFC electrolyte. Chemical interactions with the electrolyte and interconnect materials must be minimal. In addition, the cathode material must have a stable, porous microstructure so that gaseous oxygen can readily diffuse through the cathode to the cathode/electrolyte interface.

For high-temperature SOFCs operating at around 1,000°C, the preferred cathode material is A and B site doped lanthanum manganite, which offers adequate electrical conductivity and electrocatalytic activity, reasonable thermal expansion, and stability in the SOFC cathode operating environment. For SOFCs operating at substantially lower temperatures, such as 650-800°C, alternative cathode materials may be required. Alternative perovskite compositions - typically containing La on the A site, and transition metals such as Co, Fe, and/or Ni on the B site - have received attention. In general, they offer higher oxygen ion diffusion rates and exhibit faster oxygen reduction kinetics at the electrode/electrolyte interface than lanthanum manganite, but are subject to degradation of performance over time.

Approach

Selected candidate cathode materials were evaluated using a number of techniques including x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM), and x-ray photoelectron spectroscopy (XPS). The electrochemical performance was measured by sintering the cathode material onto anode-supported YSZ membranes with a samarium-doped ceria (SDC) interlayer. After attachment of current collectors, the resulting cells were placed into test fixtures and their current-voltage characteristics were evaluated using dc and impedance spectroscopy measurements. Cells were tested in air vs. moist (~3% H₂O) hydrogen at low fuel utilizations. After cell tests were completed, the cells were analyzed by SEM/EDS, and other techniques as appropriate.

Results

LSCF Cathode Degradation

While LSCF-6428 cathodes typically provide significantly higher power densities compared to LSM-based cathodes (particularly in the 600-800°C temperature range), LSCF is subject to long-term

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instability (see Figure 1). Analysis of pre- and post-tested samples indicated that segregation of Sr at the LSCF cathode interfaces may be at least partially responsible for the observed degradation of LSCF. For example, XPS data from the cathode/current collector interface, before and after testing, is presented in Table 1. It indicates significant Sr enrichment after testing. Though the Sr-rich phase may not be pure SrO, it is interesting to note that the conductivity of SrO at 750°C is very low: $\sim 5 \times 10^{-5}$ S/cm [1]. Hence, thin films of SrO formed at cathode/current collector and cathode/electrolyte interfaces could result in significant increases in ohmic resistance, and might also increase non-ohmic polarization by de-activating TPB reaction sites.

LSCF/Ag Composite Cathodes

Recently, PNNL developed a novel oxide-Ag composite cathode morphology consisting of silver spherical cores up to ~ 50 μm in diameter coated with a ~ 1 micron layer of LSCF-6428 powder. The primary

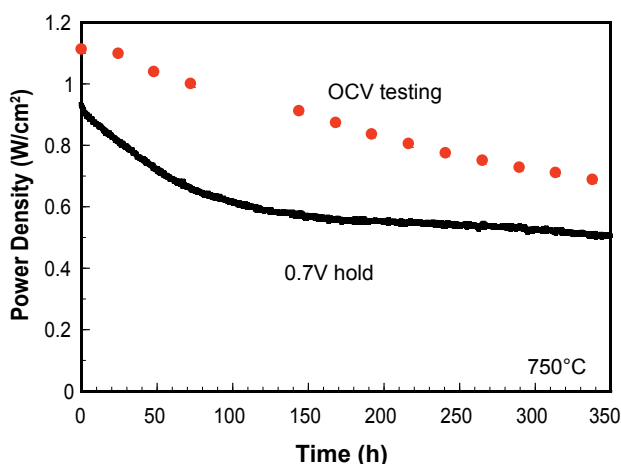


FIGURE 1. Power Density of Anode-Supported Cells Held at Constant 0.7 V, or Held at OCV Except for Brief Intermittent Testing at 0.7 V (for 5 minutes every 24 hours)

TABLE 1. XPS results for LSCF cathode surface at cathode/current collector interface. Note that Sr enrichment is greater and deeper in tested cell compared to untested or thermally annealed (but undischarged) cell.

	Surface	5 nm below surface (Ar+ ion sputtering)
Pre-Tested	29% La, 32% Sr, 35% Fe, 4% Co	45% La, 16% Sr, 36% Fe, 3% Co
Annealed (750°C/500h)	30% La, 30% Sr, 36% Fe, 4% Co	45% La, 17% Sr, 35% Fe, 3% Co
Tested (750°C/0.7V/500 h)	11% La, 68% Sr, 21% Fe	19% La, 52% Sr, 29% Fe

purpose for applying the oxide coating (via a dry coating technique known as “mechanofusion”) was the reduction of silver diffusivity and/or volatility. Figure 2 shows cross-sections of processed LSCF-coated Ag spheres; it should be noted that significantly smaller particles can be equally well coated using this technique.

Figure 3 shows $>2,000$ hours of data for a cell conditioned at 750 hours for 50 hours and then operated at 700°C. The cell exhibited additional conditioning up to 650-700 hours, and then relatively stable performance. However, degradation was observed for this cell, and a drop of $\sim 4.9\%$ in power density (at 0.7 V) was measured between 660 and 2,270 hours ($\sim 3\%$ power drop per 1,000 hours). Phenomena responsible for the conditioning and degradation characteristics of these materials have not been conclusively established, though it appears that increased contact of the coated spheres

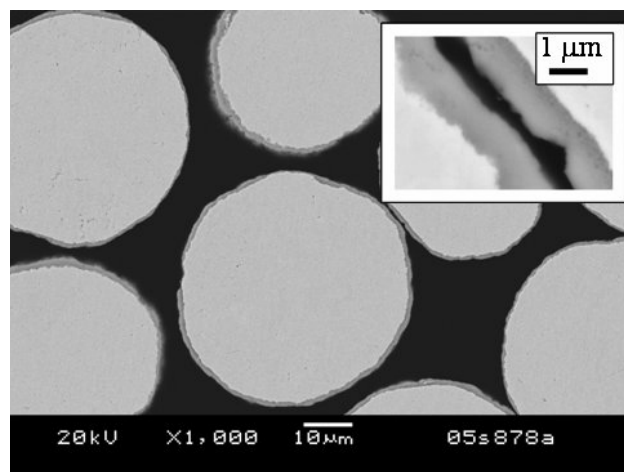


FIGURE 2. Cross-Sectional Micrograph of Silver Spheres Coated with LSCF-6428 Predominantly Indicating Excellent Coating Adhesion

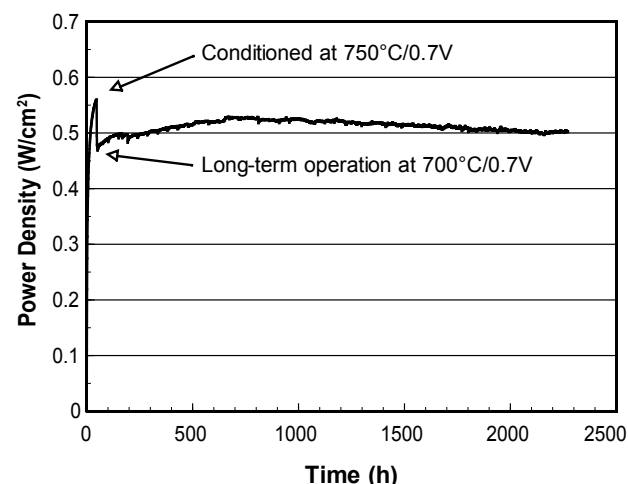


FIGURE 3. Performance Data for an Anode-Supported YSZ Cell Utilizing the Ag-LSCF Composite Cathode at 700°C and 0.7 V

along the electrolyte surface due to diffusion may play a role by increasing the cathode-electrolyte contact area. It is anticipated that optimization of the oxide composition and composite morphology may lead to improved stability. One final factor worth consideration is cost. Preliminary estimates indicate that the cost of the coated Ag-spheres is approximately 2x the cost of a typical perovskite cathode material. However, it should be noted that the use of these materials has the potential of removing two high temperature-sintering steps. First, it may be possible to sinter the cathode in situ during stack fabrication/sealing, thereby eliminating a separate sintering step at temperatures >1,000°C. In addition, preliminary results indicate that an SDC interfacial layer (and its separate sintering step) may not be required if detrimental zirconate formation is avoided at the low cathode sintering temperature (~800°C). For example, cells without the protective SDC-20 interlayer exhibited maximum power densities of ~650 and 500 mW/cm², at 750 and 700°C, respectively (tested at 0.7 V). These results are promising in that they suggest that a protective ceria layer may not be required.

Chromium Degradation Experiments

A joint study to assess Cr-related poisoning effects on standard LSM-YSZ anode-supported SOFCs was performed by a task force consisting of three organizations: PNNL, GE, and ANL. Three main types of experiments (cell performance tests with Cr vapor dosing only (Au interconnect), steel interconnect with ribs covered, and bare steel interconnect) were conducted by the task force using identical test vehicles and components. The results showed stable cell performance without chromium dosing and ~3%/1,000 hours with Cr vapor species dosing at 800°C. Much higher cell performance degradation rates were observed when the cells were in direct contact with stainless steel interconnects. Species such as (Cr,Mn)₃O₄, Cr₂O₃, and MnCr₂O₄ were identified in the cathode and near cathode/electrolyte interfaces.

Conclusions and Future Directions

- Degradation of SOFC with LSCF cathodes may be related to Sr segregation at cathode interfaces.
- LSCF/Ag composite cathodes show promising behavior at relatively low SOFC operating temperatures (e.g., 650-700°C).
- Cr vapor species in cathode air streams can have adverse effects on cell performance.
- Future work in the short term will focus on continued optimization of LSCF/Ag composite cathodes and the investigation of degradation mechanisms in alkaline earth-doped perovskite cathodes.

FY 2006 Publications/Presentations

Publications

1. S.P. Simner, M.D. Anderson, G.-G. Xia, Z. Yang, and J.W. Stevenson, "Long-Term SOFC Stability with Coated Ferritic Stainless Steel Interconnect," in Proc. 29th International Conference on Advanced Ceramics and Composites - Advances in Solid Oxide Fuel Cells (Ceramic Engineering and Science Proceedings, Volume 26, Issue 4), p. 83 (2005).

Presentations

1. "SECA Core Technology Program: Materials Development at PNNL," J.W. Stevenson, Y.S. Chou, O.A. Marina, S.P. Simner, K.S. Weil, Z. Yang, and P. Singh, SECA Core Technology Program Review Meeting, Lakewood, CO, October 25-26, 2005.
2. "State of the Art of SOFC Cathodes," J.W. Stevenson, S.P. Simner, M.D. Anderson, and P. Singh, U.S. Department of Energy Workshop: Fundamental Mechanisms of SOFC Cathode Reactions, Cocoa Beach, FL, January 22-27, 2006.
3. "Long-Term Behavior of La(Sr)Fe(Co)O₃ SOFC Cathodes," S. Simner, M. Anderson, and J.W. Stevenson, 30th International Conference & Exposition on Advanced Ceramics and Composites, Cocoa Beach, FL, January 22-27, 2006.

References

1. W.D. Copeland, *J. Phys. Chem. Solids*, 29, 313 (1968).